MicromATR

The Observation of Structural Changes in Epoxy Curing with Heated ATR Spectroscopy

Introduction

Epoxies or polyepoxides are thermosetting resins generally comprising of two parts, a component containing an epoxide ring and a hardening agent. The first epoxy resins consisted of derivatives of bisphenol-A, a widely used chemical in the polymers industry. The addition of a hardening agent to derivatives of bisphenol-A produce a reaction that involves the opening of the epoxide ring, and numerous cross links with the hardening agent. This cross-linking process creates a very rigid adhesive with numerous applications in today's modern society.

To study the chemical properties of epoxy, researchers routinely use infrared spectroscopy to understand the molecular structure and in particular, the change to molecular structure during the epoxy curing process. Attenuated total reflection (ATR) is the sampling method of choice for epoxy studies due to ease of sampling and robustness of the ATR. Diamond ATR accessories provide a distinct advantage in these studies as cured epoxy can be extremely strong and difficult to remove once hardened. The strength and chemical inertness of diamond provide the necessary physical properties for epoxy studies as the hardened product can be aggressively removed without damaging the diamond ATR.

The following discussion explores the curing process of a thermosetting epoxy using a heated diamond ATR. Understanding the curing process at various temperatures is crucial to the application of epoxy resins.

Experimental

All data recorded for this work were collected using a MicromATR (Czitek) with a heated sample plate and a commercial FTIR spectrometer. The spectra were collected using 4 cm^{-1} spectral resolution with 10 second data collection times, sampled at regular 30 second intervals. The MicromATR was fitted with a single reflection, heated diamond ATR disk. An OMEGA™ heat controller regulates and controls the heat applied to the diamond ATR. For all temperature runs and FT-IR spectra collected, the diamond ATR sampling surface was allowed to stabilize prior to applying uncured epoxy.

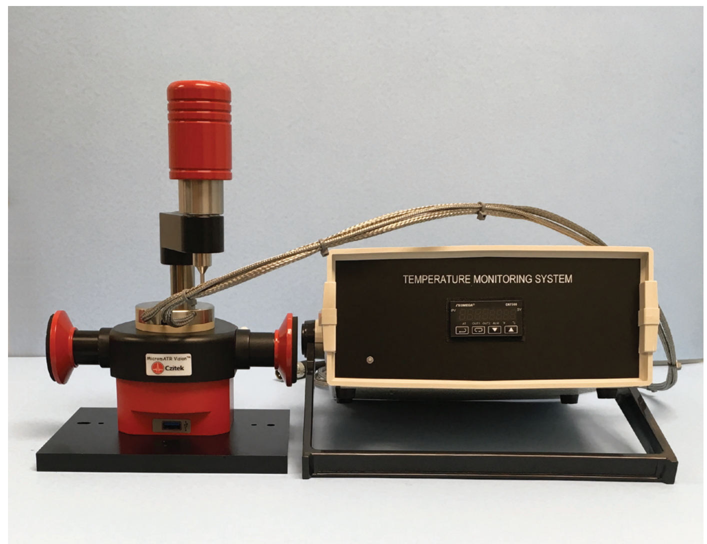

Figure 1: Temperature controller with a heated, single reflection diamond ATR on a MicromATR

The two-part epoxy EpoTek™ was mixed in a 10 (Part A) to 1 (Part B) ratio by weight. Part A contained the epoxide ring while Part B was the hardening agent. After achieving the manufacturer's recommended curing time, the epoxy was physically removed from the diamond using a razor blade. The heated ATR disk was allowed to cool to room temperature before starting the next heated temperature run.

Results and Discussion

The most noticeable difference in the IR spectra with time was the intensity loss of the absorbance band near 900 cm^{-1}, seen in Fig. 2.

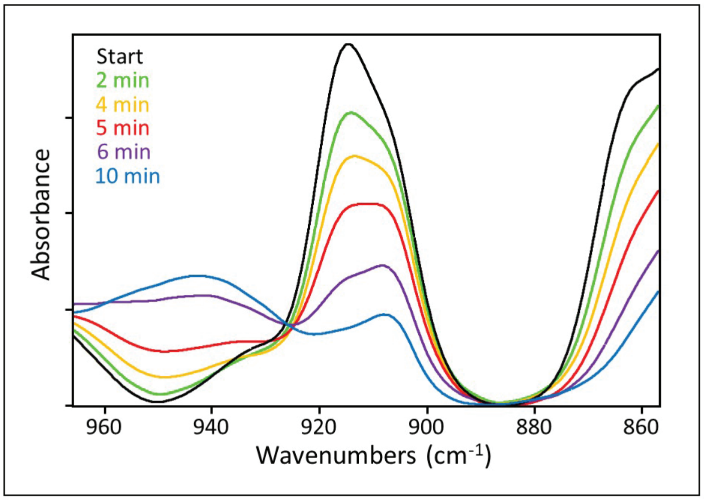

Figure 2: IR spectra showing the curing process at 100 °C

The 914 cm^{-1} absorption band is consistent with an epoxide ring stretching mode[1]. As the curing reaction proceeds, the oxirane group or epoxide ring opens and a cross links are formed with the curing agent (Part B), typically an amine containing compound. Reactions were conducted at additional temperatures to understand the influence on the rate and degree of the curing reaction.

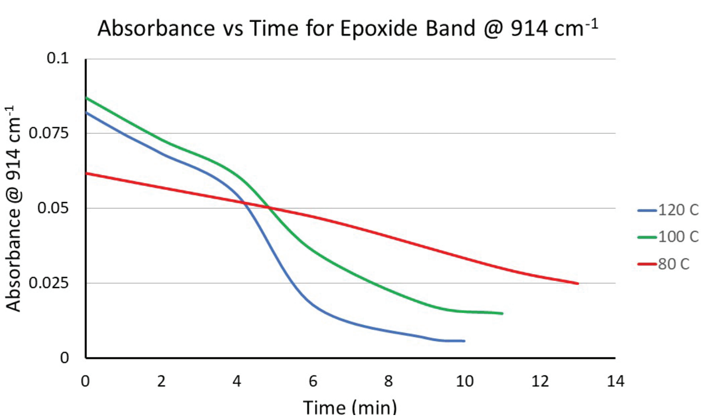

Figure 3: Epoxide band peak height as a function of time for the three temperatures tested.

Fig. 3 shows the difference in the curing process at three temperatures as a function of time. The absorbance at 914 cm^{-1} was plotted versus time in order to observe the end point of the curing process.

In the case of the 100 and 120 °C temperature runs' curing endpoint, the slope of their curves approximately reaches zero after 10-12 minutes. The 80°C temperature run still has a downward slope at the end of 13 minutes indicating the curing process has not reached its endpoint. The most notable event takes place at approximately 5 minutes in both the 100 and 120 °C runs. The sharp change in slope is indicative of a drastic structural change as the epoxide band is rapidly weakening. In general, the disappearance and emergence of bands in the IR spectrum of thermosetting epoxies can be attributed to the structural changes during the hardening process.

Conclusion

ATR spectroscopy has become a widely used and accepted sampling technique for a diverse range of applications. The addition of a heated ATR provides the capabilities to not only simplify the handling of some samples, but enables the study of reaction kinetics, and temperature induced structural changes. The superior properties of diamond with its hardness, high thermal conductivity and chemical inertness make it well suited for heated ATR applications. As seen in the study above, two-part epoxies are easily evaluated with the heated ATR, and the heat induced structural changes visualized. The combination of information rich IR spectroscopy with the ability to control sample temperature provides the tools necessary to study structural changes in thermosetting epoxides.

References:

1. Colthup, NB, Daly, LH, and Wiberly, SE, Introduction to Infrared and Raman Spectroscopy, 2nd Edn, Academic Press, NY, (1975), p.316.